

FORM PTO-1390
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. §371**

MERCK 2257

U.S. APPLICATION NO (If known, see 37 CFR §1.5)

09/857602

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PCT/EP99/09485

3 DECEMBER 1999

PRIORITY DATE CLAIMED

15 DECEMBER 1998

TITLE OF INVENTION

METHOD FOR PRODUCING MOLTEN SALTS WITH AN EXTRUDER AND USE OF THE MOLTEN SALTS

APPLICANT(S) FOR DO/EO/US

OHREM, Hans-Leonhard, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. §371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. §371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 C.F.R. §§1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. §§3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
 - a. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

IN THE UNITED STATES DESIGNATED/ELECTED OFFICE

International Application No. : PCT/EP99/09485
International Filing Date : 3 DECEMBER 1999
Priority Date(s) Claimed : 15 DECEMBER 1998
Applicant(s) (DO/EO/US) : OHREM, Hans-Leonhard, et al.
Title: METHOD FOR PRODUCING MOLTEN SALTS WITH AN EXTRUDER AND
USE OF THE MOLTEN SALTS

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

SIR:

Although the claims of the above application were amended under Article 34 during the International Phase, applicants respectfully request that the claims as originally filed by examined and this preliminary amendment is based thereon.

Prior to calculating the national fee, and prior to examination in the National Phase of the above-identified International application, please amend as follows:

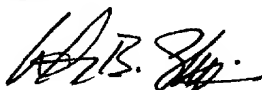
IN THE CLAIMS:

3. (Amended) Process according to Claim 1, characterized in that the reaction is carried out under reduced pressure, atmospheric pressure or superatmospheric pressure in the presence of atmospheric oxygen or, if desired, under a protective-gas atmosphere.

REMARKS

The purpose of this Preliminary Amendment is to eliminate multiple dependent claims in order to avoid the additional fee. Applicants reserve the right to reintroduce claims to canceled combined subject matter.

Respectfully submitted,



Harry B. Shubin, Reg. No. 32,004
Attorney for Applicants
MILLEN, WHITE, ZELANO & BRANIGAN, P.C.
Arlington Courthouse Plaza 1
2200 Clarendon Boulevard, Suite 1400
Arlington, VA 22201
Direct Dial: 703-812-5306
Facsimile: 703-243-6410
Email: shubin@mwzb.com

AJZ(HBS):jmm

FILED: 8 JUNE 2001

VERSION WITH MARKINGS TO SHOW CHANGES MADE

Claim 3 has been amended as follows:

3. (Amended) Process according to Claims 1 ~~and 2~~, characterized in that the reaction is carried out under reduced pressure, atmospheric pressure or superatmospheric pressure in the presence of atmospheric oxygen or, if desired, under a protective-gas atmosphere.

09/857602

11PRTS

09/857602

JC18 Rec'd PCT/PTO 0 8 JUN 2001

Process for the preparation of salt melts using an
extruder, and the use thereof

5 The invention relates to a process for the preparation
of salt melts and mixtures thereof by means of an
extruder in which the starting materials are melted and
brought to reaction, and the reaction products are
subsequently passed through a tower or column contain-
ing alkali metal salt.

10

Extruders are traditionally employed for melting and
mixing polymeric materials, such as plastics. The
extruders can also be used as reactors for
polymerizations. Anionic polymerization in an extruder
15 is described, for example, for caprolactam to nylon 6
(B. VanBuskirk, M.K. Akkapeddi, Polym. Prepr. Vol. 29,
557 (1988)). The advantage of using an extruder rather
than a stirred-tank reactor for polymerization
reactions is that it is easier to process high-
20 viscosity substances. The requirement for thorough
mixing of all substances participating in the reaction
and good heat transfer can also be achieved optimally
by using an extruder (G. Menges et al., New Polym.
Mater., Proc. Int. Semin., 129-148 (1987)). In
25 EP 813 904, pharmaceutical active ingredients are
prepared by means of extruders. Here, pharmaceutical
active ingredients carrying acid groups are reacted
with a base in the melt.

30 Melts of salts, such as, for example, NaAlCl_4 , have
various areas of application. Salt melts can be
employed as storage medium in heat stores, as heat-
transfer agents, for example in heating baths, for
covering and purifying molten metals, for electro-
35 coating of high-melting materials or as melt electro-
lyte in primary batteries, as described in
GB 2,046,506. A further possible application of these
salts is in re-chargeable sodium batteries. The salts
are employed in batteries which have operating
40 temperatures of between 130°C and 200°C (K.M. Abraham,

D.M. Pasquariello, J. Electrochem. Soc., Vol. 137. 1189-1190 (1990)).

DE 3419279 describes an electrochemical cell in which
5 the cathode matrix is impregnated with a sodium/aluminium halide salt melt electrolyte.

A relatively new area of application is the "ZEBRA
10 battery". This high-temperature cell consists of an electrode of liquid sodium, a beta-aluminium electrolyte and an electrode of transition-metal chloride in an NaAlCl_4 melt (B. Cleaver, V.S. Sharivker, J. Electrochem. Soc., Vol. 142, 3409-3413 (1995)).

15 DE 3718920 describes the preparation of salt melts by adding a pure metal and an alkali metal halide to the melt. The reaction cell is operated above the melting point of the salt melt. In the working example, the
20 alkali metal halide is NaCl , the molten alkali metal is sodium, and the separator is beta-aluminium oxide. Owing to the use of pure sodium, special safety precautions, such as working under a protective-gas atmosphere, must be taken. The reactions must take
25 place in separate cells, since poisoning of the separator by the by-product AlHal_3 formed must be prevented.

For the preparation of the alkali metal halogen
30 aluminates, the reaction of corresponding aluminium halides and alkali metal halides in a sealed tube is described (Friedmann, Taube, J. Am. Chem. Soc., 72, 2236-2243 (1950)). In this process, an increase in pressure to 6 - 7 atmospheres is observed, which
35 results in problems (FR 2168912). The apparatuses must be fitted with the appropriate safety precautions.

All the processes disclosed hitherto for the preparation of salt melts operate batchwise. A batch

procedure has some severe disadvantages compared with a continuous preparation process. During a batch change, the apparatus must be opened. The product can then be contaminated by the oxygen from the ambient air, water and dust. The batch change results in downtime of the plants and thus in a reduced space-time yield. An effective discontinuous process requires large apparatuses. The start-up process requires correspondingly more energy and time. It has been found that, in particular during start-up of the plants, impurities can be introduced into the process. FR 2168912 describes a complex purification process for alkali metal halogen aluminates. The 2-step purification process consists of oxygen treatment for degrading the organic impurities and aluminium treatment for precipitating iron and heavy metals. The aluminium treatment must be carried out under a nitrogen or argon atmosphere.

The object of the invention is to provide a continuous process for the preparation of pure salt melts which excludes the disadvantageous effects of the environment, minimizes the energy requirement and facilitates an optimum space-time yield. A further object is to make large amounts of salt melts available in the shortest possible time.

The object according to the invention is achieved by a process for the preparation of salt melts, and mixtures thereof, of the general formula



in which

35

M is Li, Na, K, Rb or Cs,

D is Al, Ga, In or Tl, and

Hal is F, Cl, Br or I,

characterized in that the starting materials, a metal
halide and an alkali metal halide, are melted and
5 brought to reaction continuously or, if desired,
discontinuously in a heatable extruder with forced
conveying, and the reaction products are subsequently
passed through a tower or column containing alkali
metal salt.

10

The process products are suitable for use as melt
electrolyte in electrochemical cells, as storage medium
in heat stores, as heat-transfer agent, for example in
heating baths, for covering and purifying molten
15 metals, for electrocoating of high-melting materials or
as melt electrolyte in rechargeable sodium batteries
and primary batteries.

Surprisingly, it has been found that the starting
20 materials can be processed by means of an extruder. It
is possible to prevent the feared contamination of the
product by abrasion by means of a suitable choice of
material and residence time.

25 It has been found that forced conveying in the extruder
by pumps can be omitted in this process, which
considerably reduces the susceptibility of the process
to faults.

30 Any extruder which appears suitable to the person
skilled in the art can be used for the process.
Particularly suitable extruders are single-screw
extruders, multiscrew extruders with co-rotating and
counterrotating screws, vented extruders, planetary-
35 gear extruders, ram extruders and disc extruders. For
the processing of salts in extruders, the hardness of
the substances employed and their chemical properties
represent particular problems which have hitherto stood
in the way of implementation. In general, the extruder

is made of steel. This material would be badly damaged by corrosion and abrasion during processing of salts.

5 It has been found that corrosion can be greatly reduced in extruders whose essential components are made of nickel alloys. It has furthermore been found that the metal parts of the extruder which come into contact with the salts or their melts can be protected against corrosive and abrasive damage by surface coatings with materials known to the person skilled in the art, such as PTFE/PFA, enamel or ceramic materials. In order to reduce abrasion, an additional bearing can be installed at the head of the screw.

15 Surprisingly, it has been found that the installation of screw elements with a reversed flow direction allows a completely molten and homogeneous product to be obtained in spite of a very short average residence time of the material in the extruder of a few seconds.

20 The reaction in the extruder can be carried out in the presence of atmospheric oxygen or, if desired, under a protective-gas atmosphere (for example nitrogen, CO₂ or noble gases) at a reduced pressure, atmospheric pressure or even at superatmospheric pressure at temperatures of from 50°C to 800°C (at atmospheric pressure). When working under superatmospheric pressure or reduced pressure, the melting points of the salts shift correspondingly and the heating stages of the extruder are modified correspondingly.

30 Processing should be carried out below the sublimation temperature of the starting materials. The reaction is preferably carried out at elevated temperatures, since the solubility of the salts is significantly better under such conditions.

During processing of the salts in the extruder, a specific choice of temperature in the heating stages

allows an optimum temperature programme to be set during the process.

5 In order to carry out the process, the aluminium halide employed is a fluoride, chloride, bromide or iodide, or mixtures thereof. Suitable alkali metal salts are lithium, sodium, potassium, rubidium or caesium fluoride, chloride, bromide or iodide, or mixtures thereof.

10

A general example of the invention is explained in greater detail below and is shown in the drawing. Fig. 1 shows a heatable extruder 1 with a solids metering device 2 and downstream column or tower 3.

15

In order to prepare salts conforming to the formula (I), and mixtures thereof, the starting materials can be fed to the extruder separately via solids metering devices 2. The starting materials can also be fed in, 20 premixed in the same ratio, via a single metering device. The extruder can also be filled under an inert gas. An extruder with forced conveying pushes the salt bed forwards in the screw channel with screw speeds of between 1 rpm and 75 rpm. The screw geometry can have 25 an l/d ratio of between 3 and 25. In the heating zones of the jacket 1, the melting temperatures for various starting materials and end products can be set. In the final quarter, it is possible to use screw elements which cause back-mixing. This increases the residence 30 time in this zone, and as yet unmelted salts are mixed with liquid melt.

The low-viscosity melt produced by the process is fed to a column or tower 3 containing the corresponding 35 alkali metal salt. The melt is passed through the alkali metal salt in order to react residual amounts of unreacted metal halide.

The conveying pressure built up by the extruder can be utilized for the transport of the melt to and through the tower or column.

- 5 The example given below is given in order to better illustrate the present invention, but is not suitable for restricting the invention to the features disclosed therein.

10

Examples

Example 1:

Preparation of NaAlCl_4

15

In order to prepare 1 kg/h of NaAlCl_4 , 373.8 g/h of NaCl is fed to an extruder via a solids metering device and 626.2 g/h of AlCl_3 is fed to the extruder via a further solids metering device. A twin-screw extruder screw with forced conveying pushes this salt bed forwards in the screw channel at a screw speed of 25 rpm. The various heating zones of the jacket can be adapted so that the salt is brought to the melting temperature of the salt during the stretch from the feed opening to the discharge zone. In the preparation of NaAlCl_4 , a temperature of 182°C is set in the feed. The final quarter contains screw elements which have a reversed conveying direction, thus increasing the residence time of the mixture in this zone. Unmelted salts are mixed with liquid melt in order to facilitate better heat transfer.

20
25
30

The low-viscosity melt formed is fed via a pipeline to a tower containing a bed of sodium chloride granules. In the tower, residues of unreacted AlCl_3 are converted to NaAlCl_4 . The conveying pressure of the extruder is sufficient to transport the melt to and through the tower without an additional pump device.

35

PATENT CLAIMS

1. Process for the preparation of salt melts, and mixtures thereof, of the general formula

5



in which

10 M is Li, Na, K, Rb or Cs,

D is Al, Ga, In or Tl, and

Hal is F, Cl, Br or I,

15

characterized in that the starting materials, a metal halide and an alkali metal salt, are fed continuously or, if desired, discontinuously via a solids metering device and melted and brought to reaction in a heatable extruder (1) with forced conveying, and the reaction products are subsequently passed through a tower or column (3) containing alkali metal salt.

20

2. Process according to Claim 1, characterized in that the starting materials are melted and brought to reaction in a heatable extruder (1) with forced conveying at a temperature between 50°C and 800°C.

25

3. Process according to Claims 1 and 2, characterized in that the reaction is carried out under reduced pressure, atmospheric pressure or superatmospheric pressure in the presence of atmospheric oxygen or, if desired, under a protective-gas atmosphere.

30

4. Process according to Claim 1, characterized in that the salt bed is processed in an extruder whose parts which come into contact with the salts or melts thereof are made of an Ni alloy or of metals coated with PTFE/PFA, enamel or ceramic materials and which

35

2025 RELEASE UNDER E.O. 14176

has a screw channel having an l/d ratio of between 3 and 25, at screw speeds of between 1 rpm and 75 rpm.

5. Use of salts of the general formula (I) according to Claim 1 as melt electrolyte in electrochemical cells and batteries.

6. Use of salts of the general formula (I) according to Claim 1 as melt electrolyte for rechargeable sodium batteries and primary batteries.

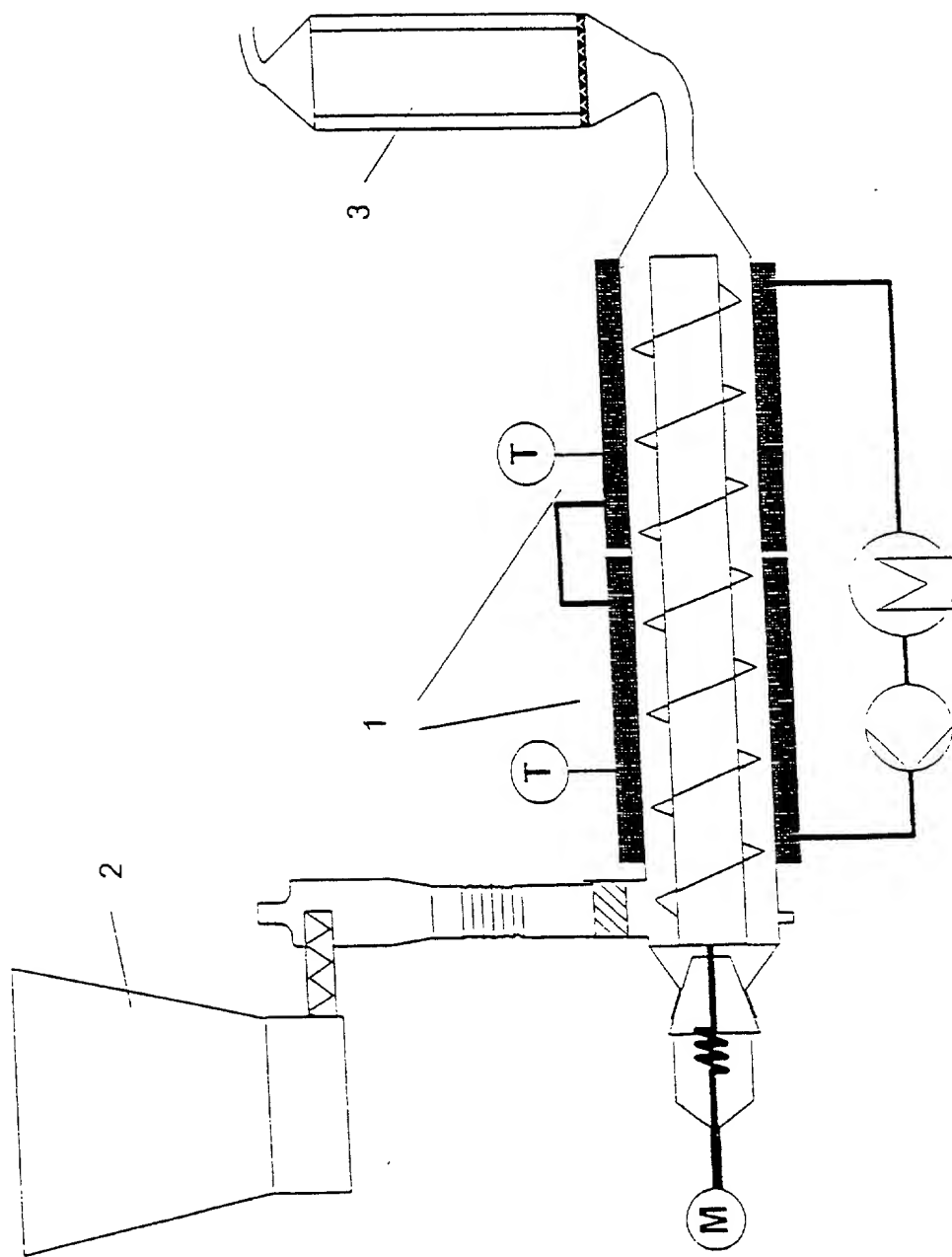
7. Use of salts of the general formula (I) according to Claim 1 as storage medium in heat stores.

8. Use of salts of the general formula (I) according to Claim 1 as heat-transfer agent.

9. Use of salts of the general formula (I) according to Claim 1 for covering and purifying molten metals.

10. Use of salts of the general formula (I) according to Claim 1 for electrocoating of high-melting materials.

FIG. 1



Docket No.
Merck

Declaration and Power of Attorney For Patent Application English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Method for producing molten salts with an extruder and use of the molten salts

the specification of which

(check one)

- ☐ is attached hereto.
☒ was filed on 03.12.1999 as United States Application No. or PCT International Application Number PCT/EP99/09485 and was amended on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

198 57 788.5 Germany 15.12.1998
(Number) (Country) (Day/Month/Year Filed)

☐

(Number) (Country) (Day/Month/Year Filed)

☐

(Number) (Country) (Day/Month/Year Filed)

☐

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U.S.C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States of PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112. I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C.F.R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint

16
I. William Millen (Reg. No. 19,544)
John L. White (Reg. No. 17,746)
Anthony J. Zelano (Reg. No. 27,969)
Alan E.J. Branigan (Reg. No. 20,565)
John R. Moses (Reg. No. 24,983)
Harry B. Shubin (Reg. No. 32,004)
Brion P. Heaney (Reg. No. 32,542)
Richard J. Traverso (Reg. No. 30,595)

John A. Sopp (Reg. No. 33,103)
Richard M. Lebovitz (Reg. No. 37,067)
John H. Thomas (Reg. No. 33,460)
Catherine M. Joyce (Reg. No. 40,668)
James T. Moore (Reg. No. 35,619)
James E. Ruland (Reg. No. 37,432)
Nancy Axelrod (Reg. No. 44,014)
Jennifer J. Branigan (Reg. No. 40,921)

to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

Send Correspondence to: MILLEN; WHITE; ZELANO & BRANIGAN, P.C.
Arlington Courthouse Plaza I
2200 Clarendon Blvd., Suite 1400
Arlington, VA 22201

Direct Telephone Calls to: (name and telephone number)

1-00
Full name of sole or first inventor

Hans-Leonhard Ohrem

Sole or first inventor's

Date

April 11, 2001

Residence

Gutenbergstrasse 6a, 64342 Jugenheim Germany DEX

Citizenship

German

Post Office Address

c/o Merck KGaA, Frankfurter Str. 250, 64293 Darmstadt, Germany

2-00
Full name of second inventor, if any

Susanne Brzezinski

Second inventor's signature

Date

April 11, 2001

Residence

Im Schafweg 5, 64683 Einhausen, Germany DEX

Citizenship

German

Post Office Address

c/o Merck KGaA, Frankfurter Str. 250, 64293 Darmstadt, Germany